CEMENT
AND
CEMENT MANUFACTURE

PUBLISHED 20TH OF EACH MONTH. PRICE 1/- A COPY. ANNUAL SUBSCRIPTION 12s. POST FREE.

PUBLISHED BY
CONCRETE PUBLICATIONS LIMITED,
20, DARTMOUTH STREET, LONDON, S.W.1.
TELEPHONE: WHITEHALL 4581.
TELEGRAPHIC ADDRESS:
CONCRETIUS, PARL, LONDON.

PUBLISHERS OF
"CONCRETE & CONSTRUCTIONAL ENGINEERING"
"CONCRETE BUILDING & CONCRETE PRODUCTS"
"CEMENT & CEMENT MANUFACTURE"
"THE CONCRETE YEAR BOOK"
"CONCRETE SERIES" BOOKS, ETC.

VOLUME 9. NUMBER 12. DECEMBER 1936

Cements with Low Heats of Hydration.

EFFECT OF PARTIAL PRE-HYDRATION AND CURING TEMPERATURES.

A series of tests to determine the effect of partial pre-hydration on the heat generated by cement while setting is described by Messrs. F. B. Hornibrook. G. L. Kalousek and C. H. Jumper in Research Paper RP-887 of the United States Bureau of Standards. Three types of commercial cements were studied, including two low-heat "Boulder Dam" cements, two high-early-strength cements, and six standard Portland cements. Samples of each of the two latter types were pre-hydrated by steam, so that the ignition losses were increased for each cement to approximately 3 per cent. and 5 per cent. respectively. The heats of hydration and also the compressive strengths of concrete specimens made of the untreated and of the pre-hydrated cements were determined for the ages of 7, 28 and 90 days and one year. Three curing conditions were used, namely, continuous storage at 70 deg. F., continuous storage at 150 deg. F., and three combinations of storage at 70 and 150 deg. F. Chemical analyses, calculated compound composition, and specific surfaces are given. The heats of hydration and compressive strengths were both reduced by pre-hydration of the cements, the 5 per cent. pre-hydration causing greater reductions than the 3 per cent. pre-hydration. At the later ages the heats of hydration obtained at continuous 150 deg. F. curing were lower than the heats obtained at continuous 70 deg. F. curing. The strengths at later ages, however, were not greatly affected by the curing temperature. Standard Portland cements, after 5 per cent. pre-hydration, had heats of hydration that would pass the low-heat specifications for "Boulder Dam" cements. The expansion results on specimens made of the untreated and of the pre-hydrated cements stored in sodium sulphate solutions show that with the exception of the cements high in tricalcium aluminate the pre-hydrations increased the resistance to the action of sodium sulphate; 5 per cent. pre-hydration resulted in greater resistance to the sulphate action than 3 per cent. pre-hydration.

The report states that some of the cracking that has occurred in mass concrete undoubtedly has been due to expansion and contraction accompanying the

excessive rise and fall of temperatures, and that these large temperature changes may be restricted by removing the heat with an integral cooling system or by the use of low-heat cements.

In a preliminary survey made at the Bureau it was found that neat cement pastes made with pre-hydrated cements evolved less heat up to 24 hours than pastes made with untreated cements. S. L. Meyers found that pre-hydration of a cement with increasing amounts of water retarded the heat evolution in increasing amounts for the first three days of hydration; with an addition of 3.58 per cent. of water the three-day and seven-day strengths were also considerably reduced. Woods[1] and Davis[2] found that cements aged in the laboratory so that the loss on ignition was appreciably increased had lower heats of hydration.

In order to obtain more comprehensive data on the effect of partial pre-hydration on the properties of cement, the Bureau studied two types of cement that were pre-hydrated with steam at atmospheric pressure so that the total ignition loss was increased in each case to approximately 3 per cent. and 5 per cent. These cements, before and after partial pre-hydration, are compared with "Boulder Dam" low-heat cements. Three types of Portland cements, comprising ten different commercial brands, were used in the investigation. Two of the group were high-early-strength, six were standard, and two were "Boulder Dam" low-heat Portland cements. The low-heat cements were composites of a number of samples of "Boulder Dam" cements passing the Bureau of Reclamation Specification 591-D. Samples of two high-early-strength and six standard Portland cements were pre-hydrated to have approximately 3 per cent. and 5 per cent. loss on ignition respectively. Complete chemical analyses and determinations of specific surface were made of all cements. The specific surfaces expressed in square centimetres per gram of cement were determined with the Wagner turbidimeter.

The partial hydration of the cements was obtained by exposing each cement to an atmosphere of steam in a rotating oven maintained at about 100 deg. C. by electrical heaters. The charge in the oven was first brought to a temperature of 100 deg. C., and the steam, which was generated in a flask at atmospheric pressure, was then passed into the oven. Because of the heat losses through the walls of the oven, the temperature in the region near the walls was below 100 deg. C. Under these conditions it was possible to pre-hydrate a cement in approximately three hours. There was some caking of the cement on the walls of the oven, but the product obtained was easily broken up. The charge, after removal from the oven, was crushed, passed through a 20-mesh sieve, and then ground in a ball-mill to the approximate fineness of the original cement. The loss on ignition was determined by the standard method.

What actually takes place during the steam hydration is not definitely known. Bied[3] found that steam treatment of "entirely siliceous cements" above 100 deg. C. did not cause them to absorb water. Artificial cements and quick-setting cements, however, absorbed water at 110 deg. C. Klein and Phillips[4] found

that the individual compounds of cement hydrated at different rates when exposed to steam. Tricalcium aluminate, at 100 deg. C. and lower temperatures, hydrated much more rapidly than tricalcium silicate, while dicalcium silicate showed no appreciable hydration with these exposures up to four hours. These compounds, in the pure crystalline form as studied by Klein and Phillips, undoubtedly behave differently than when in a heterogeneous mixture such as cement, especially since in the cement some of the alumina may be in the glass phase[5].

The two series of pre-hydrated cements are referred to as the 3 per cent. or 5 per cent. pre-hydrates. These percentages are the total loss on ignition of the respective series, and not the amount of water added by the steam treatment. Inasmuch as the original ignition losses of the cements ranged from 0.9 to 1.8 per cent., the actual amounts added by the pre-hydration treatment were correspondingly less than 3 and 5 per cent. No attempt was made to determine how much of the total water was actually combined chemically and how much was so-called "free water."

The results for heat of hydration were obtained by the heat of solution method.[1] The value for the heat of solution of the test specimen, subtracted from the value for the heat of solution of the original sample (cement or pre-hydrate), gave the heat of hydration. The results are expressed on the basis of calories per gram of the original sample of cement or pre-hydrate (not on the ignited weight basis).

Summary of Results.

(1) An increase in the loss on ignition as a result of steam pre-hydration is accompanied by a decrease in the heat of hydration. For the standard Portland cements this decrease at seven days averaged approximately 13 and 30 per cent. respectively for the 3 per cent. and 5 per cent. pre-hydrates. At one year the average percentage decrease was approximately one-half that of the seven-day decrease. For high-early-strength cements 3 per cent. and 5 per cent. pre-hydration caused an average reduction of 8 per cent. and 20 per cent. respectively at seven days, and 3 per cent. and 11 per cent. respectively at one year.

(2) The percentage reduction in heat of hydration caused by the pre-hydration of the cements was approximately the same for the 150 deg. F. curing as for the 70 deg. F. curing.

(3) The calories per gram reduction in heat of hydration for each one per cent. increase in loss on ignition varied widely between individual cements, the average reduction for all the cements at the ages of 7 and 28 days being approximately six calories, and the average reduction at one year being approximately four calories.

(4) The standard Portland cements pre-hydrated to have a loss on ignition of approximately 5 per cent. had heats of hydration at both curing temperatures for the ages of 7 and 28 days that were well within the upper limits in the specification for the low-heat "Boulder Dam" cements.

(5) Heats of hydration, calculated from empirical factors, together with

corrections for loss on ignition and specific surface, are in no case in good agreement with the observed results for ages of 7, 28 and 90 days.

(6) The cements and pre-hydrates cured continuously at 150 deg. F. had, in general, lower heats of hydration at 28 days and at later ages than when cured continuously at 70 deg. F.

(7) The cements and pre-hydrates cured in combined storage had one-year heats of hydration which compare with the results obtained at one-year storage at constant temperature as follows. (*a*) All results obtained at combined storage were lower than the corresponding results obtained at continuous 70 deg. F. storage; (*b*) for the initial 150 deg. F. curing for six days the cements and pre-hydrates had heats which, in general, were intermediate between the heats obtained for continuous storage at 70 deg. or 150 deg. F.; (*c*) for the initial 150 deg. F. storage for 27 days, the heats in general were about the same as the one-year heats obtained for continuous 150 deg. F. storage; and (*d*) for an initial 89 days at 150 deg. F. the heats in general were somewhat lower than were obtained for the continuous 150 deg. F. storage.

(8) Pre-hydration of cements results in reduction of compressive strengths, the reductions increasing with increasing ignition losses. The reductions in strength of the standard Portland cements caused by the 3 per cent. pre-hydration were, in general, approximately one-half the reduction caused by the 5 per cent. pre-hydration.

(9) Reductions in strength are greater at early ages and decrease with age. The 5 per cent. pre-hydration of the standard Portland cements caused approximately 40 per cent. reduction at seven days and approximately 20 per cent. at one year. The high-early-strength cements, although less affected by pre-hydration, follow the same trend.

(10) For continuous storage the reductions in strength caused by pre-hydration are, in general, approximately the same for storage temperatures of 70 deg. F. and 150 deg. F.

(11) The percentage reductions in compressive strengths for each one per cent. increase in ignition losses are in general greater at seven days, and then decrease with age. The 3 per cent. pre-hydrates of the standard Portland cement had in general greater proportional reductions in strength than the 5 per cent. pre-hydrates.

(12) An initial curing at high temperature (combined storage) results in lower compressive strengths at one year than are obtained with continuous curing at either 70 deg. or 150 deg. F.

(13) A comparison of the compressive strengths of the "Boulder Dam" cements with the compressive strengths of the 5 per cent. pre-hydrates of the standard Portland cement—the group that had heats of hydration that would pass specifications for low-heat "Boulder Dam" cements—shows that for 70 deg. F. curing the pre-hydrate strengths averaged 51 per cent. and 22 per cent. greater for 7 and 28 days, and 25 per cent. less for 90 days and also at one year than the "Boulder Dam" cements. For 150 deg. F. curing the pre-hydrate strengths

averaged 44, 51, 39 and 24 per cent. less at 7, 28 and 90 days and one year respectively than the "Boulder Dam" cements.

(14) Mortars of pre-hydrated and untreated cements show approximately the same expansion in water storage.

(15) Pre-hydration increased the resistance of all the Portland cements, with the exception of the two cements with the highest tricalcium aluminate content, to the disintegrating action of sodium sulphate. In general, the 5 per cent. pre-hydrates were more resistant than the 3 per cent. pre-hydrates.

(16) Mortars of untreated cements show greater expansion for leaner mixes, but no trend is indicated for pre-hydrated cements.

(17) Tests made according to the Merriman method also showed that pre-hydration increases the resistance of the cement to the action of sodium sulphate.

The results of the investigation show that pre-hydration can be successfully used to produce a low-heat high-sulphate-resistant cement without seriously impairing its other properties.

Acknowledgment is made to Mr. P. H. Bates who arranged the investigation and directed the work, and to Mr. J. Arthur Swenson who gave assistance throughout in the heat-of-hydration tests.

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Resistance of Portland Cement to Sulphate.

THE expansion of mortar prisms stored in sodium sulphate solution as the basis of an accelerated test on the effect of sulphates on Portland cement concrete has been studied at the United States Bureau of Standards. Six-inch prisms of 1-in. cross section were made from mortars of 1 : 3, 1 : 4, and 1 : 5 parts cement to standard Ottawa sand and after three days were stored in a 10 per cent. solution of sodium sulphate. The prisms were measured to the nearest tenth of a square inch before storage in sulphate solution and each week thereafter. Tests were made on forty commercial Portland cements.

These tests showed that the expansions of the 1 : 5 mortars gave the best differentiation among the different cements, and also that this differentiation was very pronounced even as early as twenty-five days after storage in sulphate solution. As a result of these tests it was suggested that cement purchased as sulphate-resisting be tested as above in the form of 1 : 5 mortar prisms and that the expansion of such bars be limited to 0.075 per cent. at twenty-five days.

Tests according to the recommended method have now been made on an additional hundred cements. Twenty-seven of these cements had expansions of less than 0.075 per cent. After six months' continued storage in the sulphate solution sixty-two of the hundred cements have completely disintegrated, and of these sixty-two only three met the requirement of the recommended test.

Chemical analyses have been made on the hundred cements and the assumed compound composition computed. Most cements with high C_3A content had high expansions at twenty-five days, and conversely most cements with low C_3A content had low expansions. Those cements with low C_3A contents but high expansions had in every case high C_3S contents.

Effects on Cement of Catalysis and Dispersion.

THE application of catalytic and dispersing phenomena to cement is described in an article by Mr. H. L. Kennedy (of the Dewey and Almy Chemical Company, Cambridge, Mass.) in a recent number of *Industrial and Engineering Chemistry*. The results show that advantages are to be obtained by such catalytic and dispersing agents and that, without changing the nature of the cements, the technique of the manufacture of cement and concrete can be improved by the addition of minute amounts of properly chosen materials.

In an effort to improve the concrete-making properties of cement, the Dewey and Almy Chemical Company has studied the effects on cement of catalysts and of dispersing and wetting agents. These studies have led to the development of a catalytic and dispersing agent which, when interground with cement, improves the desired qualities.

Microscopic examinations showed that, when wetted with water, the smaller particles of ordinary Portland cement have a strong tendency to agglomerate and

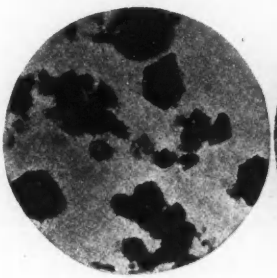


Fig. 1.

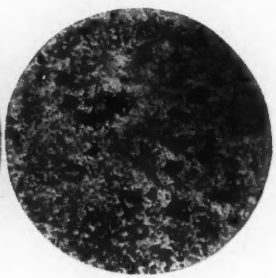


Fig. 2.

act as a large lump rather than as individual particles. *Fig.* 1 shows a dilute suspension of a standard Portland cement in water. Tests showed that the addition of a small amount of the sodium salt of certain polymers of condensed naphthalene sulphonic acid (in the early work approximately 0.1 per cent. of the weight of the cement) resulted in almost complete dispersion of the particles as shown in *Fig.* 2, a photomicrograph of the same cement at the same fineness and magnification as *Fig.* 1 but with the dispersing agent added to the mixing water.

The presence of this dispersing agent increased the workability of the resulting concrete and, by taking advantage of the water reduction thus made possible, resulted in concretes of greater strength. Obviously, if it were possible to utilise this increased workability without a water reduction and still have greater strength, a decided advance in concrete technique would result. An extensive research programme was undertaken to develop such a reagent. It was at first thought that additions which would aid the wetting of the particles might be of help. But it was later found that such was not necessarily the case and that

those agents which proved successful in solving the problem probably owed their effects to catalysis and not to wetting. Triethanolamine was eventually selected as an almost ideal agent which is effective at concentrations in the neighbourhood of 0.025 per cent. of the weight of the cement.

The action of such catalysts was found to be additive, the catalytic strength-producing agent functioning as such either with or without the dispersing agent. It was further found that not only was the development of early strength brought about by catalysis but that an increase in strength was maintained at all ages. Studies of the various properties of the concrete resulted in the formulation of a mixture of sodium and triethanolamine salts of the polymers of condensed naphthalene sulphonic acids.

The problem then arose how to add this material to the cement. Although effective when added to the gauging water at the mixer, when added to the clinker during the grinding operation the material was not only uniformly and easily distributed throughout the cement but its presence was a distinct aid to the grinding of the cement since it kept the grinding media cleaner and more effective and resulted in lower mill temperatures. In its presence, with a given rate of clinker input, the mills ground finer ; conversely, with a larger input and the same power consumption, the mills ground more clinker to the same fineness. To ensure its proper distribution and adsorption on all the cement particles (which is essential in order to realise its maximum efficiency), to prevent the removal of the dry material in the dust that is usually drawn out from the mills and also to facilitate the measuring of the comparatively minute quantities used, it was found advantageous to add the compound to the clinker in an aqueous solution. This is the present practice.

Following exhaustive laboratory tests, involving breaking more than ten thousand cylinders, mill tests with representative clinkers from the various manufacturing districts were then undertaken for the purpose of determining the action of this catalyser under both favourable and adverse commercial conditions.

Approximately ½ lb. of the original compound was used with each barrel of cement. However, although the dispersing agent itself had little or no effect upon the surface tension of its water solution, it was found that concretes made with some cements had slightly lower weights per cubic foot than those made with corresponding untreated cements. It is well known that ordinary concretes usually contain about 1 per cent. by volume of included air. The observed differences were approximately 0.7 per cent. by volume—that is, differences of about 1 lb. in the weight of a cubic foot of concrete. Although the large amount of air included when agents such as stearates and rosin are added is unquestionably detrimental, there is no evidence that any harmful effects are ever found to be due to a slight increase in air inclusion. Nevertheless, it was recognised that the ideal was a product which, while possessing all of the virtues of this original material, would not increase the included air. Consequently, a search for a new dispersing agent, which involved a study of the properties and economic

possibilities of many organic compounds, finally resulted in the selection of a derivative of lignin. In combination with the original catalytic agent, this lignin derivative resulted in a new and doubly effective material which retained all the properties of the old material without including additional air. A ¼ lb. of this material per barrel of cement is as effective as was ½ lb. of the former modification. The new agent, a mixture of triethanolamine salts and highly purified soluble calcium salts of modified lignin sulphonic acids, was offered to cement manufacturers after thorough testing, including breaking more than twenty thousand cylinders representing typical mixes with cements of widely varying characteristics and analyses from mills in all sections of the United States. Commercial experience resulted in the elimination of the older type early in 1935 and the adoption of the new formula as standard.

The use of a catalytic and dispersing agent from the manufacturing point of view is of special value in two ways. In the first place, without recourse to double burning or other expensive additional operations, it permits the manufacture of high-early-strength cements by fine grinding of most standard clinkers containing 45 per cent. or more of tricalcium silicate. In the second place, when a cement which passes all of the specifications for high-early-strength cement is not required, a catalytic and dispersing agent may be used to make cements of exceptional workability and very low bleeding tendency which have many of the advantages of standard high-early-strength cements.

Since the catalysing and dispersing agent is now being used in approximately 100,000 barrels of cement per month and has already been used in over 1,500,000 barrels, the best way to measure the extent to which it is of value is to analyse data collected during the testing of commercial cements ground at widely scattered mills. The following mill tests are reported, and, unless otherwise noted, these mill data represent runs of from 2,000 to 50,000 barrels at a time.

Strength at all Ages.

High early strength is a desirable characteristic for all types of concrete. The more completely a concrete cures during the time the mixing water is present, the stronger and more durable it becomes. On many jobs this period is limited to the time necessary to evaporate the mixing water. This is all too short in hot weather and dry climates. Cements with high-early-strength characteristics cure much farther during this limited time than do normal cements. Furthermore, where concrete is kept moist, it should continue to develop strength over long periods, and the ideal is realised when the early strengths increase constantly with continued curing.

Table I shows data for typical high-early-strength and normal cements treated by adding the material to the clinker before grinding. These were made at various times since August, 1933, at thirty different plants widely scattered over the country. All tensile data have been made in accordance with the A.S.T.M. standard procedure. All compression data were obtained using well-graded sound aggregate and, unless otherwise noted, with a water-cement-ratio of 0.80 by volume. The tensile strengths of the high-early-strength cements show

TABLE I.—TREATED COMMERCIAL CEMENTS.

Plant No.	Wagner surface area.	Tensile Strength.			Compressive Strength.*			Slump.*	Bleeding.*	Potential Composition.					
		1-day	3-day	28-day	1-day	3-day	28-day			C_3A.	C_3S.	C_2S.	C_4AF.	$CaSO_4$.	SO_3.
	Sq.cm./gram.	Pounds per square inch.								Per cent.					
							Treated High Early-Strength Cements.								
1	2,270	365	390	515	1,535	3,415	5,390	6.5	0.0	5.7	51.0	23.8	13.1	3.0	1.8
2	2,500	370	390	455	1,245	3,370	5,275	4.0	0.0	10.1	47.7	24.0	8.5	3.7	2.2
3	2,390	340	435	—	1,720	3,180	5,630	3.0	0.0	12.8	46.7	26.3	12.0	4.1	2.4
4	2,330	315	395	—	1,875	3,745	6,235	4.0	0.0	8.7	48.7	18.4	12.4	4.4	2.6
5	2,100	315	405	—	1,790	3,090	4,515	4.0	1.8	8.8	56.5	16.7	9.0	4.6	2.7
2	2,310	360	415	500	1,390	3,535	5,550	2.5	0.0	13.1	53.8	15.3	8.2	4.2	2.5
6	2,345	325	430	—	2,285	3,925	5,910	6.5	0.0	4.1	62.5	13.4	12.1	4.7	2.8
7	2,110	315	410	—	1,380	2,710	5,110	5.5	0.0	12.7	48.1	20.5	10.8	4.0	2.4
8	2,310	335	455	—	1,960	3,640	5,050	5.0	0.0	10.1	60.5	11.4	8.8	3.7	2.2
8	2,470	365	425	—	1,730	3,690	5,520	4.5	0.0	10.7	46.2	24.5	8.9	3.7	2.2
9	2,560	370	465	—	2,405	4,375	6,395	5.0	0.0	13.4	56.9	11.3	10.9	2.7	1.6
9	2,550	305	425	—	1,380	3,500	5,550	4.0	3.0	14.9	57.6	16.7	10.9	3.7	2.2
10	2,550	305	430	—	2,000	3,720	5,130	4.5	0.0	11.5	55.4	18.2	9.1	3.6	2.1
11	2,620	345	390	—	1,790	3,005	5,465	4.5	0.0	11.0	45.0	28.0	10.5	2.7	1.6
12	2,340	335	450	495	1,545	3,370	5,690	3.0	1.0	12.6	47.2	30.7	8.1	3.7	2.2
13	2,840	360	440	—	1,860	3,785	5,615	4.0	0.0	10.5	46.5	20.1	8.0	3.4	2.0
14	2,420	310	400	480	1,550	3,450	4,950	3.5	0.0	6.8	59.7	17.7	6.4	3.5	2.1
15	2,600	285	395	515	1,900	3,340	4,550	6.5	0.7	12.8	52.2	20.9	6.8	3.7	2.2
16	2,740	350	405	440	2,270	3,415	5,585	3.5	0.0	10.7	54.8	16.8	7.0	5.4	3.2
17	2,840	415	430	—	2,300	3,980	5,465	5.5	0.0	9.4	59.5	10.2	12.2	4.2	2.5
18	2,630	350	445	545	2,160	3,500	5,820	4.0	0.0	13.4	56.7	14.4	9.5	3.6	2.1
19	2,910	356	447	—	—	—	—	—	0.0	10.0	57.0	14.0	11.1	4.0	2.3
4	2,640	368	454	—	—	—	—	5.0	0.0	11.6	47.4	22.5	10.7	4.0	2.3
20	2,530	330	423	—	—	—	—	—	0.0	10.7	60.4	12.5	10.0	2.9	2.4
21	2,400	328	422	—	—	—	—	—	0.0	11.9	56.3	19.5	9.5	3.9	2.3
13	2,780	390	445	—	1,815	3,900	5,470	—	0.0	10.1	53.0	18.7	9.5	3.7	2.2
22	2,640	353	424	—	1,815	3,529	5,450	4.0	0.7	9.7	56.8	16.2	9.6	3.7	2.2
47	2,340	320	405	—	1,230	2,525	4,890	5.0	0.5	15.4	37.1	33.5	6.9	3.8	2.2
Av.	2,500	340	425	495	1,790	3,490	5,425	4.5	0.3						
Min.	2,100	285	390	440	1,230	2,525	4,515	2.5	0.0						
Max.	2,910	415	465	545	2,405	4,375	6,395	6.5	3.0						
							Treated Normal Cements.								
2	1,970	240	365	420	630	2,320	4,900	7.0	0.0	11.6	45.9	25.8	8.6	3.1	1.8
2	2,140	305	370	—	1,245	3,370	5,275	4.0	0.0	10.2	47.8	23.8	8.6	3.7	2.2
22	2,190	250	360	—	1,850	3,710	5,545	4.6	0.3	6.3	50.1	26.8	12.7	2.7	1.6
7	1,910	205	310	—	810	1,960	3,830	4.0	0.0	12.7	48.1	20.5	10.8	4.0	2.4
23	1,540	180	255	—	860	1,880	3,875	4.0	1.0	7.2	60.4	12.4	10.8	3.3	1.9
24	1,700	170	255	—	735	1,900	4,425	4.0	2.1	10.6	52.8	21.7	8.5	2.8	1.7
25	1,870	200	295	400	730	2,090	4,020	5.5	0.0	13.0	48.2	20.1	9.0	3.2	1.8
11	2,000	175	280	430	820	1,900	3,975	6.0	0.0	8.6	38.6	32.0	15.1	2.7	1.6
27	2,170	200	290	465	1,125	2,370	5,540	5.5	0.0	8.2	55.0	18.5	11.8	2.8	1.7
28	1,770	215	280	—	815	1,875	3,105	5.5	0.0	9.5	54.0	21.0	9.2	2.9	1.7
29	1,920	260	365	—	935	2,345	4,180	3.0	6.7	16.4	50.4	17.8	9.0	3.2	1.8
17	1,980	250	335	—	1,180	2,595	4,910	4.0	0.0	12.7	54.5	14.8	9.2	3.5	2.1
30	1,570	190	310	385	530	1,950	4,995	3.0	0.0	15.0	51.4	17.2	7.3	3.7	2.2
22	1,750	193	297	502	—	—	—	4.5	1.5	6.4	52.0	23.6	11.6	3.0	1.8
Av.	1,890	215	310	435	945	2,330	4,505	4.6	0.8						
Min.	1,540	170	255	385	530	1,875	3,105	3.0	0.0						
Max.	2,190	305	370	502	1,850	3,710	5,545	7.0	6.7						

* Concrete mixes, all identically graded Scituate sand and gravel, 1 to 6 by weight; water-cement-ratio (by volume), 0.80; bleeding as measured by Brown (1) at water-cement-ratio of 1.00.

TABLE II.—COMPARISON OF RESULTS ON TREATED AND UNTREATED CEMENTS.

	Wagner surface area.	Tensile Strength.			Compressive Strength.			Slump.	Bleeding.
		1-day.	3-day.	28-day.	1-day.	3-day.	28-day.		
	Sq. cm./gram.	Pounds per square inch.							
		Commercial High Early-Strength Cements.							
Untreated :									
Average ...	2,510	315	424	488	1,740	3,435	5,285	3.5	2.4
Minimum...	2,260	170	350	450	670	2,835	4,480	2.0	0.0
Maximum .	2,700	385	470	510	2,100	3,890	5,925	4.5	7.8
Treated :									
Average ...	2,500	340	425	495	1,790	3,490	5,425	4.5	0.3
Minimum...	2,100	285	390	440	1,230	2,525	4,515	2.5	0.0
Maximum .	2,910	415	465	545	2,405	4,375	6,395	6.5	1.8
		Commercial Normal Cements.							
Untreated :									
Average ...	1,630	160	285	420	635	1,865	3,710	4.0	9.9
Minimum...	1,250	50	185	345	375	1,315	2,635	1.5	0.0
Maximum .	2,120	230	345	515	990	2,740	2,840	7.1	22.0
Treated :									
Average ...	1,890	215	310	435	945	2,330	4,505	4.6	0.8
Minimum...	1,530	170	255	385	530	1,875	3,105	3.0	0.0
Maximum .	2,190	305	370	502	1,850	3,710	5,545	7.0	6.7

that the use of a catalyst permits the manufacture of high-early-strength cements from widely varying raw materials, plant locations, and potential compositions.

It is interesting to note that, with the same mix and water ratio, eight commercial untreated high-early-strength cements and twenty-two untreated normal Portland cements tested under identical conditions gave the results shown in Table II. This table also reproduces the average values from Table I. Though the average surface areas of the treated and untreated high-early-strength cements are about the same, the average tensile and compressive strengths of the treated high-early-strength cements are in every case higher than those of the untreated.

Comparing the treated and untreated normal cements, the strengths are again in favour of the treated cements. In this case, however, the average surface area of the treated cements was nearly 300 sq. cm. per gram higher than that of the untreated cements. This increase in surface area may be attributed to the presence of the addition, which acts as an efficient grinding aid and permits of the production of a cement with a higher surface area at the same mill output. Consequently, only part of the increase in strengths obtained is due to the presence of the catalyst ; the remainder is due to this increase in surface area.

Fig. 3 shows that the development of compressive strength over extended moist curing periods for various treated cements is comparable to that of untreated cements made from the same clinkers. It also shows that the early-strength advantages realised by the combined effect of finer grinding and presence of catalyst are maintained.

Durability.

Durability is perhaps the most desirable property of concrete. Freezing and thawing tests are being more and more accepted as an accelerated means of duplicating the weathering conditions to which concrete is subjected in the field.

If a concrete is not homogeneous, continued freezing and thawing inevitably cause its disintegration. If voids due to water gain under the aggregate are

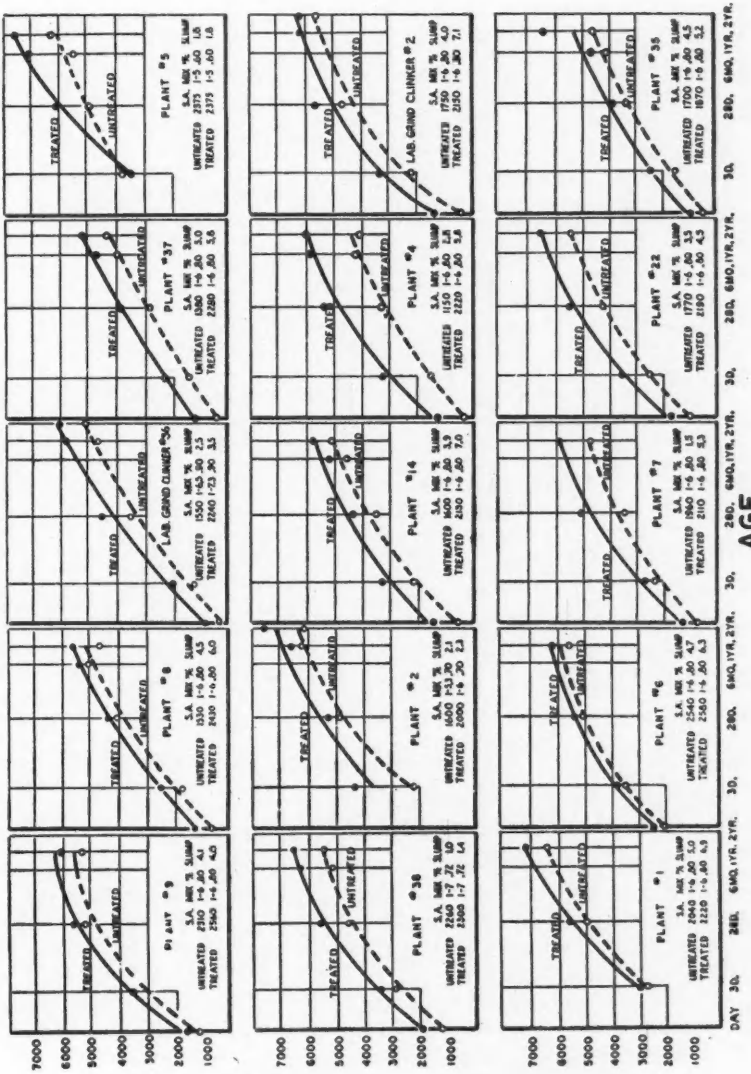
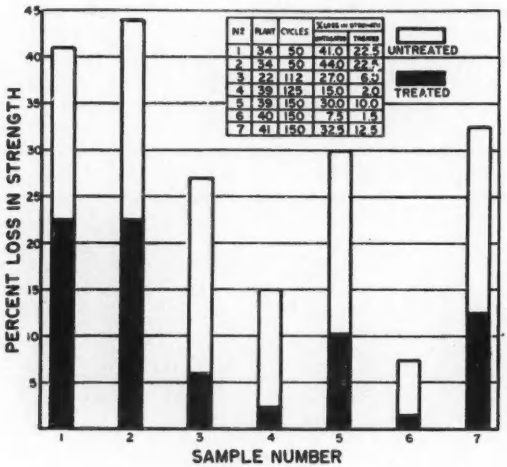

SURFACE AREAS DETERMINED BY WAGNER METHOD
COMPRESSIVE STRENGTH lbs. per sq. inch
AGE
DAY 30. 28D. 6MO. 1YR. 2YR. 30. 28D. 6MO. 1YR. 2YR. 30. 28D. 6MO. 1YR. 2YR. 30. 28D. 6MO. 1YR. 2YR.
TREATED
UNTREATED
PLANT #9
PLANT #8
PLANT #10
PLANT #2
PLANT #1
PLANT #6
PLANT #14
LAB. GRIND CLINKER #3a
PLANT #7
PLANT #37
PLANT #4
LAB. GRIND CLINKER #2
PLANT #22
PLANT #5
PLANT #35

Fig. 3.

present, water fills these channels during the thawing cycles and, upon freezing, causes strains which hasten disintegration.

Fig. 4 compares graphically the resistance to freezing and thawing of several typical concretes made with cements treated with this material and of those made with normal cements of identical or less fineness from the same clinkers. These data are presented with full appreciation of the fact that they are far from complete and in the expectation that a future paper will deal exhaustively with this property and its relation to bleeding. However, preliminary work carried on at several independent laboratories shows that concretes made with cements treated with this addition are much more resistant to freezing and thawing than



NO	PLANT	CYCLES	% LOSS IN STRENGTH UNTREATED	% LOSS IN STRENGTH TREATED
1	34	50	41.0	22.5
2	34	50	44.0	22.4
3	22	112	27.0	6.5
4	39	125	15.0	2.0
5	39	150	30.0	10.0
6	40	150	7.5	1.5
7	41	150	32.5	12.5

Fig. 4.

concretes made with corresponding untreated cements ground to the same or lesser fineness.

Workability.

There is probably more controversy over the measurement of " workability " of concrete than over that of any other characteristic of concrete. Several methods of testing workability have been devised, but unfortunately results obtained from these different methods frequently fail to agree in practice. Consequently, as is generally admitted, no satisfactory and accurate method of measuring workability of concrete is yet available. Research is now in progress, and it is hoped that a satisfactory test procedure will shortly be developed and that a paper devoted to this subject can be presented in the near future. Although physical measurements are not available because of this situation, those who have used treated cements (whether ground very fine to pass high early-strength specifications or ground less fine) on works agree that they are very workable.

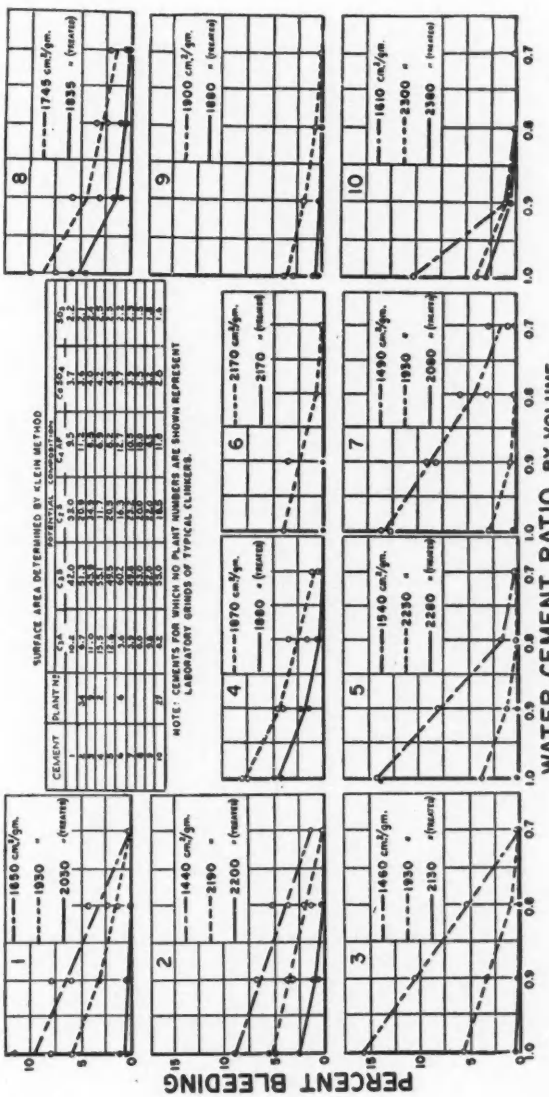
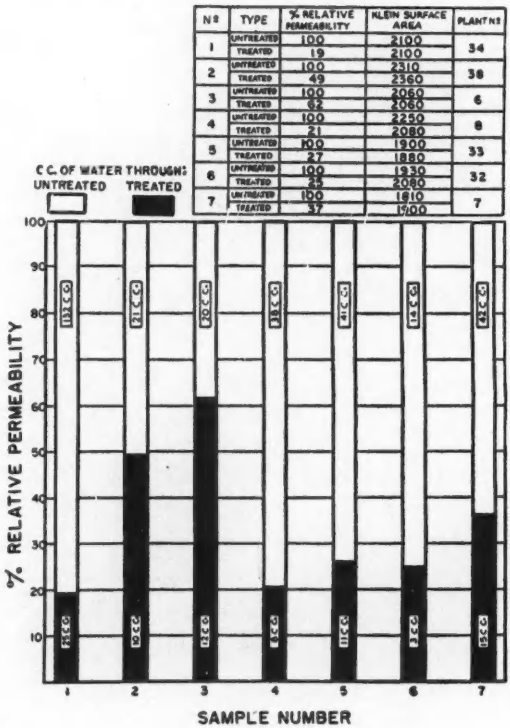

PERCENT BLEEDING
WATER CEMENT RATIO BY VOLUME
SURFACE AREA DETERMINED BY KLEIN METHOD
NOTE: CEMENTS FOR WHICH NO PLANT NUMBERS ARE SHOWN REPRESENT LABORATORY GRINDS OF TYPICAL CLINKERS.

Fig. 5.

Negligible Bleeding.

The cause of "bleeding," a detrimental characteristic of concrete only recently fully appreciated, is to-day the subject of much discussion. Throughout this paper the term "bleeding" is used to designate the separation of water from the cement paste before the cement is hard. Brown (1) has published a full discussion of the subject.



No	TYPE	% RELATIVE PERMEABILITY	KLEIN SURFACE AREA	PLANT No
1	UNTREATED	100	2100	34
	TREATED	19	2100	
2	UNTREATED	100	2310	38
	TREATED	49	2360	
3	UNTREATED	100	2060	6
	TREATED	62	2060	
4	UNTREATED	100	2250	8
	TREATED	21	2080	
5	UNTREATED	100	1900	33
	TREATED	27	1880	
6	UNTREATED	100	1930	32
	TREATED	25	2080	
7	UNTREATED	100	1810	7
	TREATED	37	1900	

Fig. 6.

Bleeding, as discussed quantitatively here, refers only to this characteristic of cement itself. It is reflected in the bleeding of the resulting concrete. Up to a certain point the bleeding tendency of a cement is usually reduced by increasing the fineness, but in many cases, after commercial fineness is obtained, bleeding is still excessive.

Excessive bleeding results in three objectionable characteristics of concrete: (1) the formation of voids under the aggregate, sometimes called "water gain" under the aggregate; (2) non-homogeneous concrete, due to the difference in density between the top and bottom of a section of concrete caused by the rise

of water towards the surface ; and (3) excessive laitance. The beneficial effect of the addition is especially notable with cements of high bleeding characteristics. *Fig.* 5 contrasts graphically the bleeding characteristics of various cement pastes made with ten typical treated and untreated but otherwise identical cements. However, in studying these data it is to be remembered that there are a few normal untreated cements and a larger number of untreated high-early-strength cements which show negligible bleeding characteristics.

Permeability to Passage of Corrosive and Pure Waters.

Methods of quantitatively measuring water percolation through concrete are not fully developed, but progress in this direction is being made. There is already evidence that the permeability to transverse flow is greatest where high bleeding tendencies have accentuated water-gain layers under the aggregate.

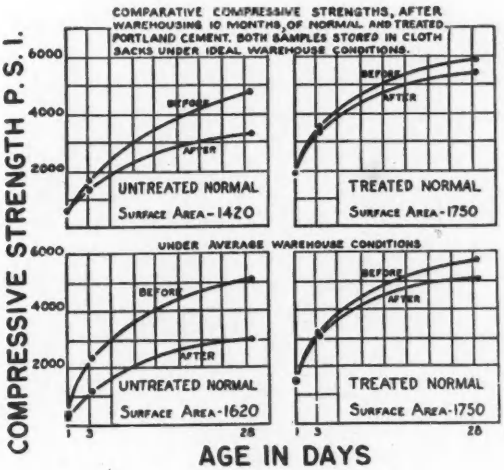


Fig. 7.—Storage data.

Fig. 6 is a graphical comparison of the relative permeability of seven typical treated cements and the corresponding untreated normal cements. The method used to obtain these results was to pour 2-in. by 4-in. porous mortar cylinders, having a mix of 1 to 5 by weight, around the ends of ½-in. steel tubes 10 in. long. After hardening, these porous cylinders were cast inside of 8-in. by 12-in. concrete cylinders. After curing for 28 days, water at a pressure of 50 or 100 lb. per square inch was forced into the projecting tubes. The permeability of the concrete specimens was measured by the amount of water forced into the cylinders.

This method is as yet far from completely satisfactory ; many cylinders are prone to so much leakage along the tubes that the data from such tests must be discarded. However, the results shown here are from only such tests as were

TABLE III.—COMPARATIVE GRINDING RESULTS.

Plant No.		Grinding Rate.			Wagner Surface Area.			1-day Tensile Strength.			3-day Tensile Strength.			1-day Compressive Strength.			3-day Compressive Strength.			28-day Compressive Strength.		
		Untreated.	Treated	Per cent. increase.	Untreated.	Treated.	Per cent. increase.	Untreated.	Treated	Per cent. increase.	Untreated.	Treated	Per cent. increase.	Untreated.	Treated.	Per cent. increase.	Untreated.	Treated.	Per cent. increase.	Untreated.	Treated.	Per cent. increase.
		Bbl. per hr.			Sq. cm. per gram.			Pounds per square inch.														
		High Early-Strength Cement, Equal Grinding Rates.																				
1		15	15	0	2,040	2,220	9	225	305	36	315	380	21	1,290	1,645	27	2,600	3,020	16	4,495	5,240	17
1		15	15	0	2,100	2,270	8	260	305	17	340	390	15	1,340	1,535	15	2,760	3,415	24	4,805	5,390	12
3		57	57	0	2,050	2,390	17	190	340	79	325	435	34	840	1,720	105	2,710	3,180	17	3,690	5,630	53
2		32	32	0	2,020	2,315	15	290	360	24	415	415	0	875	1,390	59	3,260	3,535	8	5,510	5,550	1
8		36	36	0	2,420	2,470	2	285	365	28	405	425	5	910	1,730	90	2,575	3,690	43	4,585	5,520	20
12		22	22	0	1,910	2,340	22	225	335	49	390	450	15	1,095	1,545	41	2,650	3,370	27	4,730	5,690	20
14		45	45	0	2,340	2,420	3	275	310	13	380	400	5	1,290	1,550	20	3,270	3,450	6	4,800	4,950	3
16		28	28	0	2,150	2,740	27	250	350	40	360	405	12	870	2,270	161	2,820	3,415	21	4,610	5,585	21
	Av.	42	42	0	2,130	2,395	13	250	335	36	365	415	13	1,060	1,670	65	2,830	3,390	20	4,050	5,340	18
		Normal Cement, Equal Grinding Rate.																				
2		59	59	0	1,850	1,970	7	185	240	30	335	365	9	375	639	68	2,310	2,320	0	4,840	4,900	1
7		100	100	0	1,810	1,910	6	205	205	0	335	310	−7	745	810	9	2,220	1,960	0	3,610	3,830	6
22		135	135	0	1,520	2,060	36	157	280	78	335	380	13	680	1,240	83	2,100	3,490	66	3,900	5,200	33
24		38	38	0	1,460	1,700	21	135	170	26	345	255	4	445	735	65	1,445	1,900	31	3,540	4,425	25
27		180	180	0	1,770	2,170	23	140	200	43	270	290	7	820	1,125	37	1,380	2,370	72	3,140	5,540	76
28		41	41	0	1,620	1,770	9	185	215	16	260	280	8	620	815	31	1,545	1,875	21	2,635	3,105	18
17		43	43	0	1,830	1,980	8	230	250	9	285	335	18	750	1,180	57	1,930	2,595	34	3,135	4,910	57
30		61	61	0	1,470	1,570	7	155	190	23	270	310	15	505	530	5	1,530	1,956	27	3,080	4,995	62
	Av.	75	75	0	1,660	1,890	15	174	219	21	282	315	8	618	883	39	1,820	2,310	26	3,490	4,610	35
		High Early-Strength Cement, Increased Grinding Rate with the addition.																				
6		90	108	20	2,320	2,380	3	330	325	−2	430	430	0	2,070	2,285	10	3,370	3,925	16	4,980	5,190	4
8		40	64	60	2,540	2,310	−9	340	335	−1	420	455	8	2,100	1,960	−7	3,680	3,640	−1	5,185	5,050	3
9		40	65	62	2,360	2,560	8	345	370	7	435	465	7	1,970	2,405	18	3,830	4,375	14	5,795	6,395	10
13		12	24	52	2,420	2,840	17	330	360	9	435	440	1	1,380	1,860	35	2,835	3,785	33	4,480	5,615	25
17		20	38	90	2,750	2,850	4	330	415	26	380	430	13	1,905	2,300	21	2,820	3,980	41	5,170	5,465	6
22		44	69	51	2,470	2,485	1	260	350	35	415	425	2	680	1,240	82	2,100	3,490	66	3,900	5,200	33
22		75	75	0	1,750	2,470	41	200	315	58	345	395	14	440	860	96	2,075	3,075	48	4,390	4,520	30
	Av.	41	61	49	2,370	2,550	9	305	353	19	408	434	5	1,510	1,845	36	2,960	3,750	30	4,840	5,350	16
		Normal Cement, Increased Grinding Rate with the addition.																				
11		22	30	36	2,030	2,000	−1	135	175	30	265	280	6	545	820	51	1,550	1,900	23	3,795	3,975	5
29		100	125	25	1,580	1,920	21	200	260	30	345	365	6	970	935	−4	2,240	2,345	5	3,390	4,180	23
	Av.	61	78	30	1,805	1,960	10	168	218	30	305	323	6	758	878	23	1,895	2,120	14	3,590	4,075	14

free from such leakage ; in each test the concretes made with treated cements were much less permeable than those made with the corresponding untreated cements.

Storage Qualities.

When stored in warehouses in bags, cements have a tendency to form lumps. This tendency is a function of the fineness of the cement and the moisture present during storage ; the finer the cement, the greater is the tendency to form lumps. If these lumps become hard, they are not properly broken up during mixing, and the resulting concrete is dangerously non-homogeneous. But before lumping becomes severe, cement usually passes through an intermediate stage where more water is required to make a given concrete workable ; there is, in consequence, a loss of strength.

Fig. 7 shows comparative strengths obtained after storing typical treated and the corresponding untreated cements in sacks for ten months under ideal and average conditions. In each case the loss in strength of the treated cements was considerably less than that of the normal untreated cements.

Grinding.

Table III shows results obtained at a number of plants making high-early-strength cement and normal cement, treated and untreated at equal grinding rates. When the grinding rates were equal, a considerable increase in the surface area was obtained. When maintaining approximately the same surface areas, the output of the treated high-early-strength cements was, on the average, almost 50 per cent. greater than that of the corresponding untreated high-early-strength cements ; with the less finely ground treated normal cements the output was 30 per cent. greater than with corresponding untreated cements.

Entrained Air.

A study of any addition to cement which does not measure the effect that such an addition has upon the amount of air included in concretes made with the resultant cement is incomplete. Depending upon (1) the workability, (2) the nature of the aggregate and cement, and (3) the mix, normal concretes contain from 0.5 to 2 per cent. of entrained air. Much of this normally entrained air is in the form of fine emulsified globules of the air originally in the interstices of the cement and has not been shown to be detrimental. On the other hand, those who have worked with grinding aids, such as rosin and stearates, have found that abnormal amounts of air (sometimes as high as an additional 6 per cent.) are included, with consequent detrimental effects on the strength and durability of the resulting concretes.

Table IV shows the amount of air, expressed as a percentage by volume, included in identical concretes made with typical untreated normal and high early-strength cements and with the same cements when treated. The column headed " Calculated Density " shows the theoretical absolute weight per cubic foot of the mix as calculated from the absolute volumes of the aggregates,

cement, and water used. The column headed "Observed Density Untreated" shows the actual weights per cubic foot found by weighing 7-day cured cylinders in air and water. The columns headed "Entrained Air" show the difference in these two densities expressed as included air. In these data the large amount of air (approximately 3.5 per cent.) in the untreated normal cement from plant No. 8 is inexplicable; because of the possibility that it may have been due to accidental

TABLE IV.—COMPARATIVE AIR ENTRAINMENT.

Plant No.	Calculated density.	Observed density untreated.	Density treated.	Entrained Air.		Treated decrease Per cent.
				Untreated.	Treated.	
	Pounds per cubic foot.			Per cent. Absolute volume.		
	Normal Cements.					
1	154.45	153.45	153.25	0.6	0.8	−0.2
2	154.45	151.00	151.15	2.2	2.1	0.1
4	154.45	152.81	153.00	1.1	0.9	0.2
8	154.45	149.05	153.75	3.5	0.6	2.9
13	154.45	153.05	153.35	0.9	0.7	0.2
14	154.45	152.45	153.05	1.3	0.9	0.4
15	154.45	152.25	152.65	1.4	1.1	0.3
18	154.45	152.35	152.65	1.4	1.2	0.2
22	154.45	149.15	150.45	3.4	2.6	0.8
23	154.45	152.75	153.00	1.1	0.9	0.2
26	154.45	153.05	153.25	0.9	0.8	0.1
33	154.45	152.25	152.65	1.4	1.1	0.3
42	154.45	151.65	151.55	1.8	1.9	−0.1
43	154.45	153.45	153.15	0.7	0.8	−0.1
44	154.45	152.95	153.05	0.9	0.9	0.0
45	154.45	151.85	152.25	1.7	1.5	0.2
46	154.45	151.75	153.75	1.7	0.5	1.2
18	154.45	152.65	152.95	1.1	1.0	0.1
	Average*	152.29	152.66	1.4	1.2	0.2
	Maximum*	153.45	153.75	3.4	2.6	2.9
	Minimum*	149.15	150.45	0.6	0.5	−0.2
	High Early-Strength Cements.					
8	154.45	152.75	152.90	1.1	1.0	0.1
9	154.45	152.30	153.65	1.4	0.5	0.9
12	154.45	152.10	153.60	1.5	0.6	0.9
13	154.45	152.95	152.30	0.9	1.4	−0.5
14	154.45	153.05	153.80	0.9	0.4	0.5
47	154.45	153.25	153.10	0.8	0.9	−0.1
	Avefage	152.73	153.22	1.1	0.8	0.3
	Maximum	153.25	153.80	1.5	1.4	0.9
	Minimum	152.10	152.30	0.8	0.4	−0.5

* Omitting Plant No. 8.

contamination of the cement with some oily matter, this figure is omitted from the averages.

These data are of interest not only because they show that it has been possible to find an agent which has the beneficial effects shown by the preceding data and does not have any tendency to increase air inclusion, but also because the original type of catalytic and dispersing agent increased the entrained air in identical concrete by about 0.7 per cent. by volume.

REFERENCE.

[1] Brown, L. S., *Ind. Eng. Chem.*, 27, 97 (1935).

Tests of Hot Cement.

DUE to the fineness to which modern cements are ground, the cement on issuing from the mill may attain a comparatively high temperature and be delivered at a fairly high temperature. Sometimes, especially in hot weather, cement may become heated during transit, and may appear as if it had been hot when loaded.

There are differences of opinion, states L. Krüger (*Zement*, 1936, page 741), as to whether hot cement adversely affects the properties of concrete with which it is made. Hot cement will attain normal strength only if it passes the setting-time test. The German State Railway Administration requires, when concreting is done in frosty weather and the gauging water and aggregate must be heated,

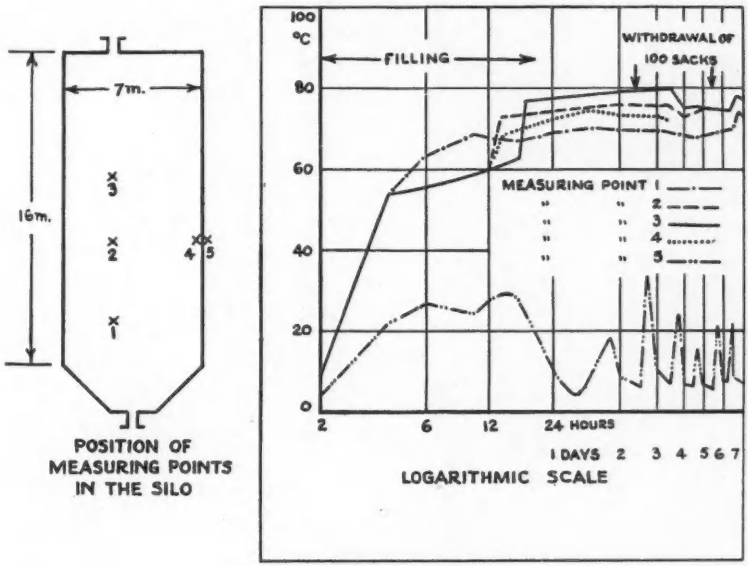


Fig. 1.

that the cement should be put into the mixer only when the mixture of aggregate and water is not hotter than 35 deg. C., otherwise the cement may set too quickly.

The following tests for hot cement are described by the author.

Tests should be made at the cement works during the grinding of the clinker, the temperature at which the clinker enters the mill and the temperature of the cement at the exit from the mill and in the silo being measured. Tests on freshly-ground cement according to the standard specification will indicate the setting, soundness, and hardening properties of hot cements. Strength tests on concrete made with cement at various high temperatures, and also with aggregates

which have been cooled or heated, should be carried out. Finally, investigations at the building site during hot weather will determine the temperature at which the cement was delivered and the conditions prevailing during the making of the concrete.

Tests were made at a cement works and in the laboratory during the production of normal Portland cement at the beginning of November, 1935. The outside temperature at night was about 5 deg. C. and rose to about 20 deg. C. during the day. The clinker on the feed-table before the mill had a temperature of 58 deg. C., and the temperature of the cement on leaving the mill was 81 deg. C. In the conveyor screw (which was somewhat long) there was no cooling. The temperature of the cement in the silo is given in *Fig.* 1. The charging lasted about twenty-two hours. The cement was discharged into the silo, which had cooled overnight, and its temperature during the first two hours was about 10 deg. C. After filling to point 1 (*Fig.* 1) (about one-quarter of the total depth) the temperature after a further two hours was about 55 deg. C. and the air temperature in the silo had risen to about 65 deg. C. When the silo was half-filled the temperature of the cement and air was 70 deg. C. After twelve hours a constant temperature was reached at any particular measuring point. No conduction of heat at a distance of 35 cm. from the silo wall could be observed. Loosely-packed cement in a silo is a very bad conductor of heat and cools very little even after comparatively long periods (observations were made up to ten days) so long as it is not drawn off.

For carrying out the standard tests, the required amount of cement was taken after a hundred sacks of cement had been drawn off. The temperature of the cement was 53 deg. C. Some was put in a thermos flask and some in the original sacks which were taken to the testing station in an insulated box so that there was no loss of temperature. As it was desired to test as many hot cements as possible, the temperatures of cements during the filling of other silos were measured. As a second test, a cement with a temperature of 73 deg. C. which had lain two days in the silo was taken.

Table 1 gives the results of the tests. First the cement paste was made with cement at temperatures of 53, 40, 30 and 20 deg. C. and water at 20 deg. C. The

TABLE 1.

Test	Temperature (Deg. C.)			Temp. rise 1 min. after gauging.	Temp. rise after setting (Deg. C.).	Initial setting time.		Final setting time.		Soundness.
	Cement	Water	Cement paste.							
No.						Hrs.	Mins.	Hrs.	Mins.	
1	53	20	28.6	0.5	0.5	4	—	6	—	Sound
2	40	20	27.2	0.4	0.4	4	45	5	45	Sound
3	30	20	24.7	0.3	0.3	4	45	5	45	Sound
4	20	20	21.4	0.3	1.8	3	45	5	—	Sound
11	72	18	32.0	0.7	0.7	4	15	5	—	Sound
12	40	30	30.3	0.4	0.4	4	—	5	—	Sound
13	30	30	27.8	0.2	0.2	4	30	5	30	Sound
15	19.2	18	20.8	0.5	6.0	5	—	5	45	Sound

temperatures of the pats were between 28.6 and 21.4 deg. C. A rise in temperature after setting occurred, as was expected, only when the cement and water were mixed at room temperature. No speeding-up of the initial set was observed. The shortest initial and final setting times were obtained at normal temperatures. The cements were sound according to both the preliminary and the final tests. The second sample at 73 deg. C. gave somewhat shorter initial and final setting times, if the cement was used at this temperature, compared with the setting times when it was used at normal temperature. Speeding-up of setting times occurred also with cement at 40 and 30 deg. C. and water at 30 deg. C.

The results of the strength tests are given in Table 2. In these tests cements at various high temperatures were used with standard sand and water at 30, 20

TABLE 2.

Test No.	Temperature (Deg. C.).				Strengths in kg. per sq. cm. Standard Mortar.				Water storage. Plastic Mortar.		
					7 Days.		28 Days.		28 Days.		
	Cement.	Sand.	Water.	Mortar.	Tension.	Compression.	Tension.	Compression.	7 Days' bending tensile strength.	Bending tensile strength.	Compression.
01	53	20	20	19	26.0	331	31.4	421	42.3	52.3	305
02 21	40	20	20	19	25.3	317	30.1	414	40.5	49.3	245
03 11	30	20	20	20	27.6	328	29.8	427	38.8	49.2	316
04	20	20	20	20	27.0	351	31.0	437	36.8	48.6	295
12	30	30	30	20	27.7	337	31.7	440	45.0	50.7	353
13	30	5	5	19	29.9	357	35.7	461	43.9	50.6	293
22	40	5	5	19	29.0	350	34.4	466	43.7	49.5	253
31	72	19	19	20	29.7	361	36.5	463	40.7	50.5	343
32	19	19	19	20	29.9	479	32.5	571	47.9	56.5	435

and 5 deg. C. For the cement taken at 53 deg. C. the seven-day strength (especially the compressive strength) was somewhat lower than the standard test at normal temperatures if used at over 20 deg. C. The standard tensile strength is practically the same. Specimens made from plastic mortar with mixed sand gave somewhat higher strengths for hot cements with one exception, namely, the compressive strength of cement at 40 deg. C. If the cement at 40 deg. C. is made up with sand and water at 20, 30 and 5 deg. C. (compare tests Nos. 21 and 22, and also Nos. 11 to 13, with test No. 04), a similar effect is observed. The tensile strength, and, usually, also the compressive strength, were higher (as would be expected) for cement and sand or water at higher temperatures than for standard mortar at normal temperatures. For the cement at 73 deg. C. only two sets of tests (Nos. 31 and 32) were carried out. The standard strength of the cement was somewhat higher than for the cement at 53 deg. C. The tensile strengths, according to the standard specification, of the hot cement and of the cement at 20 deg. C. did not

show any uniformity (see tests Nos. 31 and 32). The twenty-eight-day tensile strength at normal temperature is very low. The bending tensile strength of the plastic mortar is lower for the hot cement than for the cement at 19 deg. C.

The compressive strength of the standard mortar, and also of the plastic mortar made with hot cement, was about 16 to 20 per cent. below that of cement at normal temperature. This fall of strength occurred only in the case of this one test ; further tests to be carried out may give an explanation of this.

Even as the standard tests of cement cannot really give its behaviour in concrete, so also in this case the results of the mortar test cannot be directly applied to concrete. This is shown by the results of the tests on concrete (see Table 3) for which cement at 73 deg. C. was used. The concrete contained

TABLE 3.

Test No.	Concrete with 300 kg. of cement per cubic metre. Temperature in deg. C.				Stiffness with 12 per cent. water content. Spread in centimetres.	Strength in kg. per sq. cm. after 28 days.	
	Cement.	Aggregate.	Water.	Concrete Mixture.		Bending tensile strength.	Compressive strength.
01	73	72	85	43	34/36	40.2	388
02	60	20	20	25	41/42	37.3	381
03 11	30	20	20	22	40/40	43.7	357
04	20	20	20	20	41/40	34.2	394
12	30	30	30	30	38/38	40.9	359
13	30	30	30	30	37/38		
				24	34/35	42.2	350

300 kg. of cement per cubic metre, and the water content was about 12 per cent. The temperature of the mixture varied according to the temperature of the cement, sand, and water ; in these cases there were necessarily greater differences of temperature. This is seen when tests Nos. 01, 12 and 13 are compared with tests Nos. 02 to 04. Up to test No. 12 the specimens were kept for the first seven days in warm air at 30 deg. C. under damp cloths, according to the standard German method for reinforced concrete. The concrete mixture for test No. 13 was left for 2½ hours after mixing before it was used and was worked up again before being made into beams and cubes ; temperature and workability had dropped.

The lowest bending tensile strength was obtained for concrete made at 20 deg. C. ; in all other cases it was higher by up to 25 per cent. The compressive strengths of the concretes of tests Nos. 01, 02, and 04 are practically equal. The concrete cubes from mixtures at 43 and 20 deg. C. had the same high compressive strength. Concrete made with cement at 30 deg. C. showed a drop in compressive strength of about 20 per cent. Even though the fall has scarcely any practical meaning, it should be noted that in the tests made so far for cements at 30 deg. and 40 deg. C. the results are irregular.

From these tests there seems to be no disadvantage in using cements which have a temperature up to 70 deg. C. and which at the same time have an initial set longer than three to four hours.

Recent Patents Relating to Cement.

Concretes.

445,264. Anderson, D., Cropthorne, Brand Hall Road, Langley, near Birmingham. Aug. 1, 1934.

Aluminous cement of low iron content is mixed with fused or sintered alumina and water; the composition sets to form a hard stone useful for making dies and moulds. The alumina may be in the form of corundum or emery or a synthetic product such as those known as Alundum, Aloxite, and Bauxilite. Preferably a substantial portion of the alumina should be in the form of fine powder. Fillers may be added. According to the first provisional specification, the alumina may be in the form of Scottish lateritic rock or hæmatite ores or electro-furnace abrasives produced from bauxite, and the cement, alumina and water may be mixed under vacuum.

Concretes.

452,863. Bjorkman, E. B., 296, High Holborn, London. Dec. 31, 1934.

A material for addition to a concrete mix of Portland cement, aggregate, and water is made by disintegrating into drops and simultaneously chilling a molten mass of calcium alumino silicates having such chemica composition that the quotient

$$\frac{CaO + MgO + \frac{1}{3}Al_2O_3}{SiO_2 + \frac{2}{3}Al_2O_3}$$

is not higher than 1.5 and not lower than 1.0, and grinding the solidified particles thus obtained to greater fineness than Portland cement. The additional material is stated to reduce the heat generation during setting, to lower the solubility of the set concrete, and to improve the strength of the concrete when it replaces not more than 70 per cent. by weight of the Portland cement. Solidified particles having a diameter greater than about ¼ in. are stated to be unsuitable for further treatment and are preferably removed before grinding. The fineness is normally such that 5 per cent. of the ground material is left on a sieve having 200 meshes to the inch. Molten blastfurnace slag having the required chemical composition or adjusted to provide the required chemical composition may be used for the manufacture of the admixture.

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Cements.

445,164. Krupp Grusonwerk Akt.-Ges., Buckau, Magdeburg, Germany. July 12, 1935.

Cement is made by mixing blastfurnace slag with fuel and raw materials which give hydraulic properties, e.g. cement raw meal or limestone meal, the materials containing, or there being added, only sufficient moisture to yield a mixture in the form of grains or lumps, calcining the mixture on a constantly or periodically working grate, air being passed through the mixture after it has been ignited, and then grinding the calcined material. Wet-granulated or dry air-granulated slag may be used.

Cements.

446,952. Krupp Akt.-Ges., Essen, Germany. Oct. 9, 1935.

Cement clinker is made by finely grinding some of the raw material, mixing it with coarser-grained raw material, and sintering the resulting mixture. The coarser-grained material must have sufficient strength to withstand conversion into clinker without the grains being broken to smaller size, sufficient porosity to enable it to be mixed intimately with the finely-ground material, and must contain sufficient moisture for the fine grains to stick to the coarser grains throughout the treatment. The fine material may be limestone and the coarse material may be foamy slag such as that prepared as described in Specification 294,175, slag sand, pumice, lava, or tuff, but not ordinary blast furnace slag, which is too soft. Powdered fuel may be mixed with the fine material.

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448,477. Soc. Anon. Française Eternit, Prouvy-Thiant, Nord, France. March 15, 1935.

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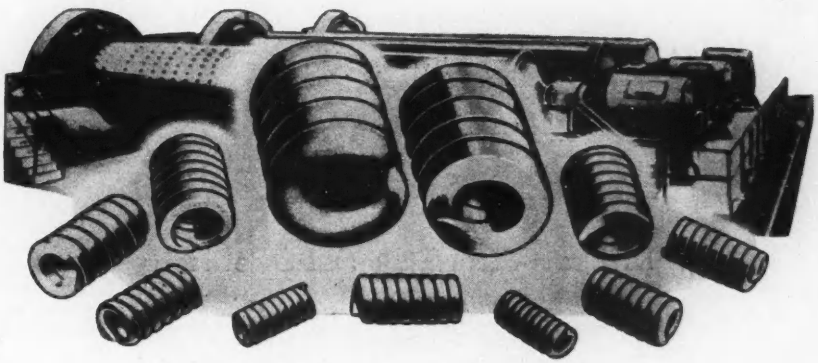

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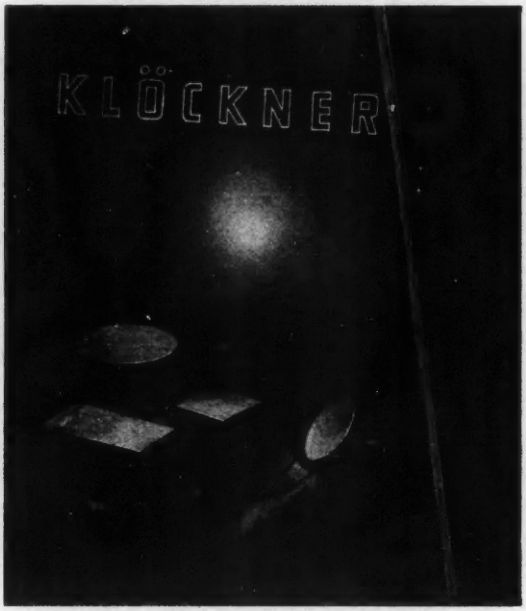

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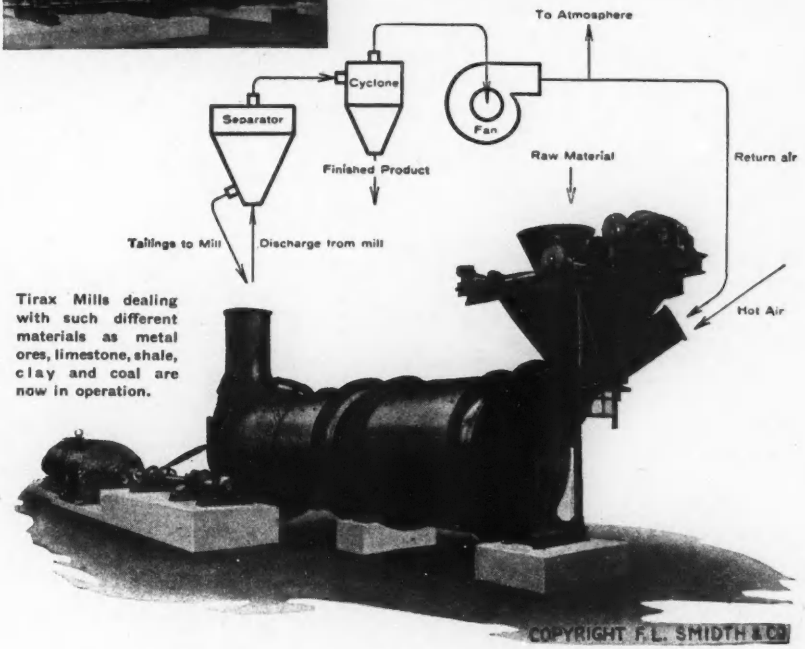

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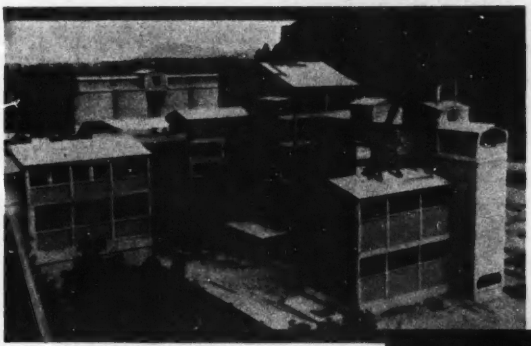

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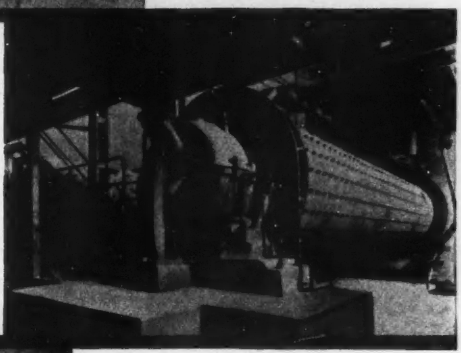

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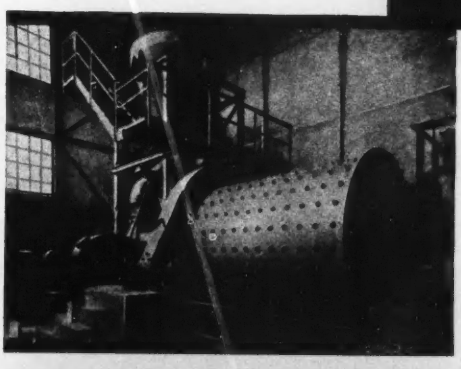

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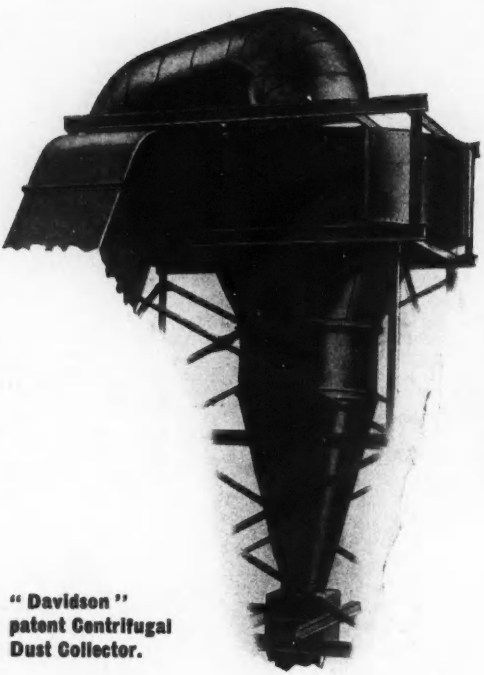

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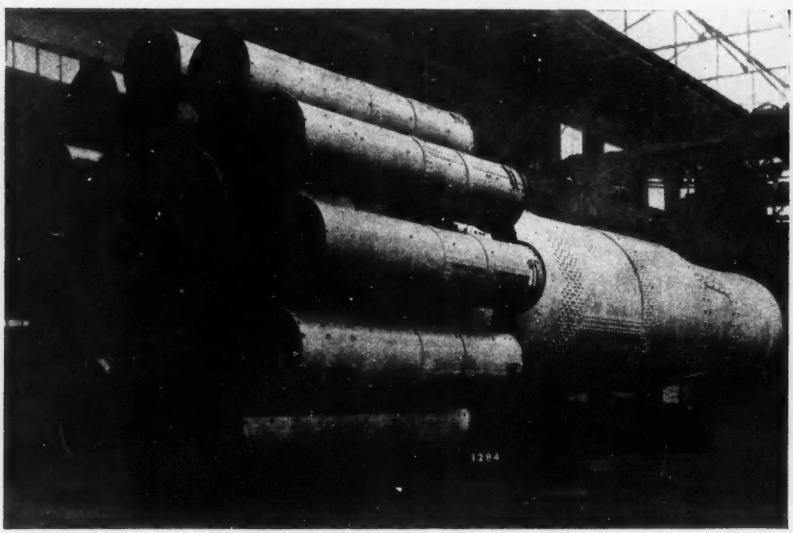

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